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(54) CLEAR PERFUMED POLYAMIDE RESIN AND METHOD OF MAKING IT

(71) We, POLAK'S FRUTAL WORKS, INC., a corporation of the State of New York, United States of America, of the City of Middletown, New York, New York 10904, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to materials composed of clear substantially solvent-free polyamide resins containing perfume oils and to methods of making the same. By 'solvent-free' we mean free from solvent other than the resins and perfume oils themselves.

Polyamide resins are known which vary from clear to opaque and from smearable semisolids to very hard bodies of high tensile, compressive and impact strength.

It has been proposed to make perfumed objects of soft gels containing polyamide resin, e.g., a clear lipstick that can be smeared on the lips and a clear candle that on burning volatilizes the perfume and adds fragrance to the atmosphere around it. In these products the polyamide is used in relatively small proportions as a gelling agent in a system which otherwise contains a large proportion of solvent liquid, a dye or pigment, and a relatively small amount of fragrance. The gels are soft, spreadable and deformable at room temperature.

It has been discovered that a clear solid, i.e., relatively rigid, polyamide resin material containing perfume oil can be made without substantial amounts of added solvent by proper selection of the polyamide resin and by following certain making procedures as set forth hereinbelow.

According to the present invention we provide a clear solid thermoplastic resin material consisting substantially of a thermoplastic polyamide resin containing perfume oil in an amount not exceeding 30 per cent by weight based on the resin plus the perfume oil, and being substantially free of solvent, said thermoplastic polyamide resin being a fatty polyamide which softens within a range of 10 to 15°C on heating in the range of 100—200°C., has a sharp decrease in viscosity at temperatures above its softening range and has a molecular weight within the range 6000 to 9000.

The resin used in the invention must be optically clear at room temperature to yield an optically clear body containing perfume oil. In general the polyamide resins having this desired clarity and suitable physical properties are fatty polyamides which have molecular weights within the range of 6,000 to 9,000 and are based on condensation of polyamines, especially diamines and triamines, with high molecular weight dicarboxylic acids, especially of the type which result from dimerization of diunsaturated carboxylic acids, e.g., condensation products of dimerized linoleic acid and ethylene diamine. They are charactedized by substantial retention of their room temperature hardness on heating until very near the melting or softening temperature which is relatively sharp, e.g., over a range of 10—15°C. within the range of 100 to 200°C., depending on the molecular weight, and by a sharp decrease in viscosity at temperatures above the melting or softening point or range. The optical clarity is believed to be due to the solubility of all of the components in the resin. Methods of making such resins are disclosed in the expired U.S. Patent 2,379,413. In contrast, some well known polyamide resins of the nylon type, e.g., nylon 6, which are not suitable for the present invention have higher molecular weights and are opaque, probably because the components of the mixtures are not mutually soluble.

A clear resin suitable for use in the invention is made by reacting dimerized linoleic

acid with ethylene diamine to produce a product of the formula

$$HO(—OC—R—CONHR^1—NH)_nH$$

in which R is a hydrocarbon group of an indeterminate configuration containing 34 carbon atoms and R^1 is $—CH_2CH_2—$ and which has the following typical properties:

Softening point (Ball and Ring)	110—115°C.
Viscosity (Brookfield)	
Poises at 150°C	30—35
Poises at 160°C	21—27
Tensile Strength (P.S.I.)	1500—2000
Color (Gardner, 40% solution)	4—7
Specific Gravity	0.97

It is clear amber in color, non-tacky at room temperature, has a relatively sharp melting point and is thermoplastic with a narrow heat seal range. It exhibits good adhesion to a variety of substrates and can be applied to substrates from solution or from a melt. Thin films show good flexibility. The resin is conveniently prepared for commercial use in diced form for supplying either batch heating vessels or molding machines. Such a resin in diced form is available commercially from General Mills, Inc., under the name Versamid 930 ("Versamid" is a registered Trade Mark). Versamid 940 is similar thereto but has slightly lower viscosity, tensile strength and elongation. Versamid 1635 also is similar thereto but has a lighter color and lower inherent color. Resins having these properties are excellently suitable for the present invention. Further description of the suitable resins is unnecessary because they are well known to those skilled in the art and have been extensively described in literature published by General Mills on Versamid polyamide resins, in text books, encylopedias, and other technical publications.

The fragrances suitable for the present invention, sometimes called perfume oils, are complex mixtures of volatile compounds ing esters, ethers, aldehydes, alcohols, unsaturated hydrocarbons, e.g., terpenes, which are well known to persons skilled in the fragrance art and need not be further identified. Their use as to type and proportion in the present invention is limited only by solubility in the resin to produce a clear product.

The process of making the clear perfumed resin materials of the invention comprises melting the resin by heating it until sufficiently molten to be stirrable and pourable. For a resin having the properties specified above this condition obtains when the temperature is within the range of 100—200°C., and preferably below about 160°C. The perfume oil is added to the liquid resin and blended therewith, e.g., by stirring or other mechanical agitation until a uniform mixture or blend is formed. No solvent for the resin and the perfume oil need be added at any time during the process. The mixture is cooled promptly after thorough mixing to solid condition, preferably rapidly as by quenching in cold water or by pouring onto or bringing into contact with a cold metal surface to which it is not adherent. The product obtained by this process is optically clear, has a high polished surface and a strong fragrance that faithfully represents the odor of the perfume oil, especially when the resin used has low inherent odor. These products have good optical stability and retain a substantial proportion of the fragrance for months.

The perfumed materials of the present invention may be formed into a wide variety of useful objects such as jewellery, e.g., pendant earrings, pins or brooches; decorative castings such as birds, animals, or abstract objects; coatings on various substrates, e.g., on Christmas tree ornaments and electric light bulbs such as Christmas tree lights where the heat of the lighted filament increases the volatility and rate of transfer to the atmosphere of the perfume oil from the resin coating. Such coated Christmas tree ornaments and lights can be scented with pine oil, for example, to add an aspect of reality when used on artificial Christmas trees.

The proportion of perfume oil to resin may vary from small but effective amounts of the order of a percent or so up to the maximum amount the resin can contain and still maintain optical clarity which is up to 30% by weight based on the resin plus the perfume oil. In general it is preferred to use about 12% which is an optimum value balancing the proportion of perfume oil recovered in the product against the length of time period over which the objects give off a fragrant odor.

The following specific Example illustrates the method and product of the invention.

Example

In a vessel associated with a source of heat a quantity of diced Versamid 930 amounting to 88 parts by weight is heated to about 130°C. at which temperature the resin is a pourable and stirrable body of liquid. A quantity of a perfume oil having a floral bouquet with a woody background amounting to 12 parts by weight is stirred into the liquid resin until a uniform blend is achieved at which time the mixture is poured into standing cold water to facilitate rapid cooling and solidification to minimize loss of perfume oil. The product is clear amber solid having a highly polished surface

with a pronounced odor faithfully reproducing the fragrance of the perfume oil used in making it. The product is in the form of a solid solution which lends itself to molding under heat and pressure into objects of jewellery such as pendant earrings, to casting in molds to form decorative art objects, and to spreading as a film on substrates such as Christmas tree ornament or glass light bulbs. Similar results are achieved using Versamid 1635 and other perfume oil fragrances.

In general it is advantageous to carry out the mixing operation in a closed vessel, preferably a pressure vessel, in order to prevent substantial loss of perfume oil by vaporization. Where the final objects are made by molding, e.g., injection molding, the perfume oil is preferably introduced directly into the resin in the feed supply line, preferably after the resin is liquified, and uniformly blended into the resin therein.

WHAT WE CLAIM IS:—

1. A clear solid thermoplastic resin material consisting substantially of a thermoplastic polyamide resin containing perfume oil in an amount not exceeding 30 per cent by weight based on the resin plus the perfume oil, and being substantially free of solvent, said thermoplastic polyamide resin being a fatty polyamide which softens within a range of 10 to 15°C on heating in the range of 100—200°C., has a sharp decrease in viscosity at temperatures above its softening range and has a molecular weight within the range 6000 to 9000.

2. A resin material as claimed in Claim 1, in which the perfume oil is in the resin as a solid solution.

3. A resin material as claimed in Claim 1 or 2, which is part of a piece of jewellery.

4. A resin material as claimed in Claim 1 or 2, which is in the form of a decorative casting.

5. A resin material as claimed in Claim 1 or 2, which is a coating on a substrate.

6. A resin material as claimed in Claim 5, in which the substrate is in the form of an ornament.

7. A resin material as claimed in Claim 5, in which the substrate is in the form of an electric light bulb.

8. A clear polyamide resin material according to Claim 1, substantially as described with reference to the foregoing Example.

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